

PROCESSING OF LEATHER WASTE: PILOT SCALE STUDIES ON CHROME SHAVINGS. PART II. PURIFICATION OF CHROME CAKE AND TANNING TRIALS

ABSTRACT

The knowledge acquired in chromium recovery and recycling from waste water has been applied to the recovery of chromium from solid wastes. These wastes were first treated to recover as much protein as possible, and then chemical treatment was used to purify the chrome cake for recycle. This second part discusses the purification of the chrome cake and its reuse in tanning trials. Matched sides comparisons were done with seven hides, varying the proportion of recovered chromium to virgin chromium from 0 to 100%. Chemical analyses in the wet blue stage and physical tests in the crust stage were performed on all the leather samples to evaluate the tannage.

INTRODUCTION

Up to 40% of the chromium used in the tanning process can be discharged with the waste water. There are basically two methods of reusing chromium from tannery waste water:^{1,2} recycling the purified exhausted chrome liquor as a pickling float for the next batch³⁻¹⁴ and precipitation, also known as recovery.¹⁵⁻¹⁹ In spite of advantages of chrome precipitation,

it requires costly equipment, and only chrome liquor recycling is commonly applied in most parts of the world.²⁰

The common way of recovering chromium is precipitation, but many other methods have been proposed in the literature; one is incineration,²¹ including incineration of chrome shavings and leather scraps. The recovery of chromium from solid tannery wastes has also been studied by methods such as air oxidation,²² extraction,²³ incineration,^{24,25} and hydrolysis.²⁵

Since chromium recycling and chromium recovery, either from waste water or solid waste, have been used in the tanneries, the extent to which chromium recycling influences the properties of the resultant leathers has been debated. Matched side investigative comparisons have been made with recycled chromium, demonstrating that the influence on the final leather produced from recycled chromium was nil to very low, when compared to conventional chrome tanning.¹²

This knowledge, acquired in chromium treatment, has been used in the recovery of chromium from solid wastes. These wastes were first treated to recover as much protein as possible, and then chemical treated to purify the chromium for recycle.^{26,27}

In the first paper of this series,²⁸ protein products were isolated from chrome shavings in four pilot plant trials. Commercial chrome shavings were digested, with an initial alkali step and with an alkaline protease second step, to isolate two different protein products: gelatin and hydrolysate. Chemical and physical properties of these protein products and chemical properties of samples of the solid residue from each step of the process samples were measured.

In this second part, the treatment of the chrome cake to purify the chrome for reuse in the tanning trials are presented. Matched sides comparisons were done with seven sides, varying the proportion of recovered chromium to virgin chromium from 0 to 100%. Chemical analyses, such as moisture, ash and chrome content in the wet blue stage, and physical tests in the crust stage were performed on all the leather samples.

EXPERIMENTAL

Materials

Chrome shavings were obtained from a commercial tannery in two different drums and were stored at room temperature. Sulfuric acid, sodium hydroxide (50%, w/w soln.), and ammonium hydroxide were obtained from Fisher Scientific (Fair Lawn, NJ), sodium sulfide, lime, soda ash, sodium sulfhydrate, ammonium sulfate, sodium chloride, sodium formate, sodium bicarbonate, Oxochrome, wattle, Daxad 17 LPH, formic acid, and Avalanfixb were obtained from Tannin Corp. (Peabody, MA), Borron TS was obtained from Röhm Tech., Inc. (Malden, MA), Proxel was obtained from Chemtan Co. (Exeter, NH), Rohapon 6000 was obtained from TFL USA/Canada, Inc. (Greensboro, NC), Phenolphthalein was obtained from Rohm and Haas Co. (Philadelphia, PA), Busan 30 was obtained from Buckman Laboratories, Inc. (Memphis, TN), DLE syntan and Baysyntan NNOL were obtained from BASF Corp. (Charlotte, NC), Atlasol CAM, Eureka 400R, and Atlasol 310L were obtained from Atlas Refinery, Inc. (Newark, NJ), and the dye used was Sandozol Brown FCT powder from Clariant Corp. (Charlotte, NC).

Procedures

Treatment of chrome shavings. Chrome shavings were treated, as described in a previous paper,²⁸ to isolate gelatin and hydrolysate protein products. A chrome cake was obtained as a by-product.

Treatment of chrome cake. The diagram of the procedure used can be found in Figure 1. Chrome cake (132 kg) was

dissolved in 98% sulfuric acid (20.68 kg; 23% of weight of initial chrome shavings) until the pH was 1-1.2. Then, the pH of the solution was slowly raised to 1.9-2.1 with 50% w/w sodium hydroxide soln. (6 kg; 6.6% of weight of initial chrome shavings). The solution was heated to 60°C and held at temperature for 30 min and was allowed to cool and stand overnight at room temperature. The solution was then filtered through Büchner porcelain funnels with filter paper #1. The retentate was sampled and discharged. The filtrate was adjusted to pH 9 with 50% w/w sodium hydroxide soln. (6.75 kg; 7.5% of weight of initial chrome shavings). The solution was heated to 70°C and held at temperature for 2 hours and allowed to cool and settle for 2 to 3 hours. The solution was then filtered with a conventional filter press and the cake was washed with water. Samples of the cake, the filtrate and the wash were taken.

Adjustment of basicity. The purified chromium precipitate was redissolved in 98% sulfuric acid. Approximately 3.57 kg (1950 mL, 4.0% of weight of initial chrome shavings) was needed to dissolve the chromium and to adjust the pH of the resulting solution to 2.3 (the pH of pickled sides). The chromium content of the solution was 30 g/L. By diluting a portion of that solution, an artificial tanning bath could be prepared with a desired amount and concentration of chromium.

Tanning trials. Matched sides trials were set up to test the tanning capability of the recovered chromium. Seven fresh cattle hides were collected from a commercial slaughter house. They were halved, trimmed, fleshed, soaked, unhaired, relimed and delimed, bated, pickled, tanned and neutralized, retanned, and dyed using the process listed below:

Soak	100% Water @ 80°F (26°C)
	0.15 % Borron TS
	0.10% Proxel
	Run continuously @ 6 rpm for 2 hrs, drain.
Wash	100% Water
	Run @ 6 rpm for 5 min, drain.
Unhair	100% Water @ 85°F (29.5°C)
	2% Na ₂ S
	2% Lime
	1% Soda ash
	Run @ 6 rpm for 4 hrs, tumbling 10 min every hour, drain.
Wash	100% Water
	Run @ 6 rpm for 5 min, drain.
Relime	200% Water @ 80°F (26°C)
	1% NaHS

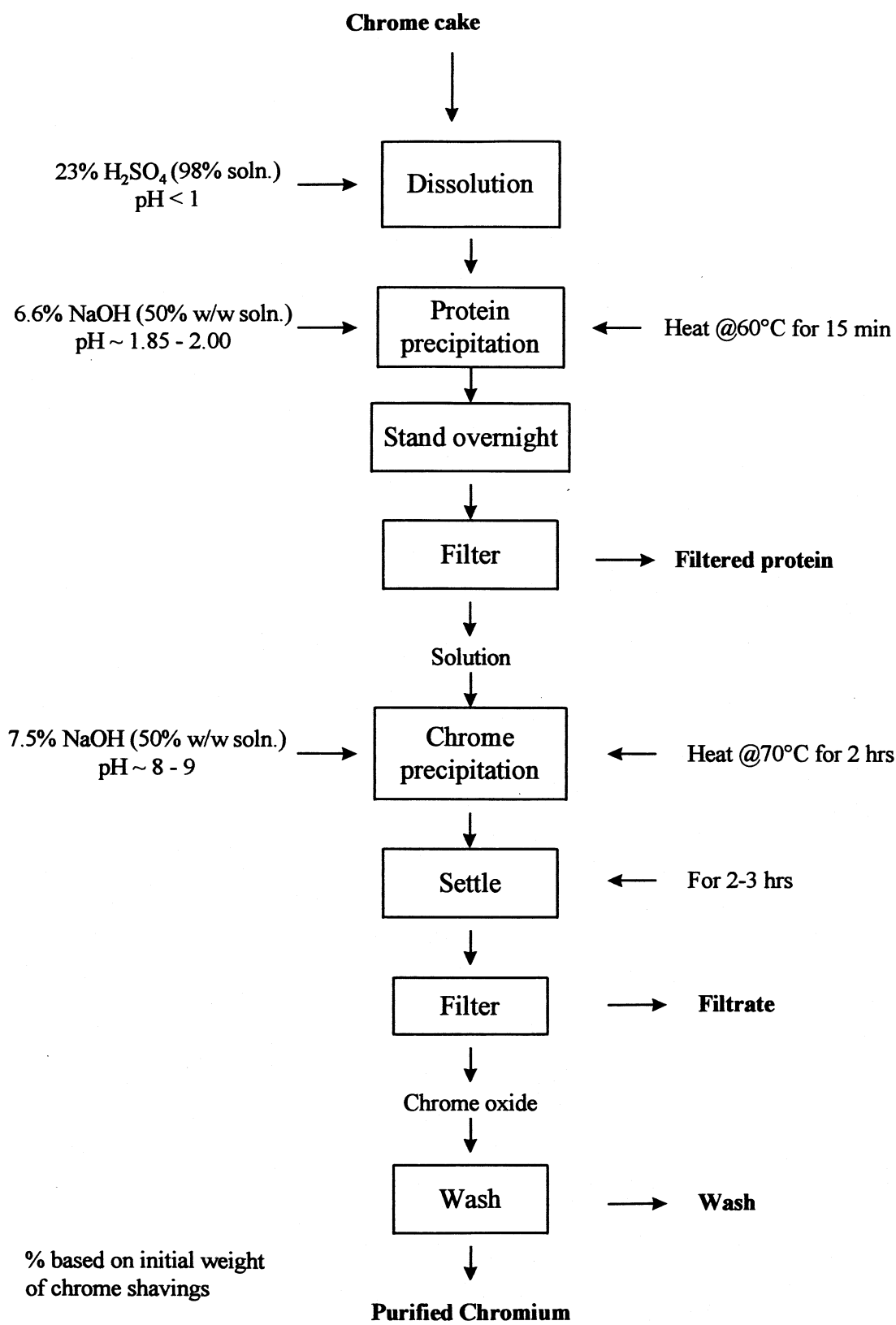


FIGURE 1. — Flow diagram of the procedure for purification of chrome cake.

2% Lime
Run @ 6 rpm for 20 hrs tumbling 3 min every hour, drain.

Wash (Twice) 100% Water
Run @ 6 rpm for 5 min, drain.

Delime-bate 125% Water @ 90°F (32°C)
3% Ammonium sulfate
0.15% Rohapon 6000
0.10% Borron TS
Run continuously @ 6 rpm for 90 min, drain.
Target pH=8.8-9.0
Check lime streak with Phenolphthalein (1/3 pink in center).

Wash 100% Water
Run @ 6 rpm for 5 min, drain.

Pickle 0% Water @ 80°F (26°C)
3% Sodium chloride (add salt through the drum door)
Run continuously @ 6 rpm for 5 min.
2% Sulfuric acid
8% Water for dilution
Run continuously @ 6 rpm for 2 hrs.
Target pH = 1.8, target Baumé = 5.

Tan 75% Water @ 80°F (26°C)
0.75% Sodium formate
8% Oxochrome
5% Sodium chloride
0.1% Busan 30
Run continuously @ 16 rpm for 4 hrs, raising the temperature from 80 to 110°F (26-43°C).

Basification 2% Sodium bicarbonate
24% Water
Run continuously @ 16 rpm until pH 3.8 with running water @ 100°F (38°C) for 10 min, drain.

Wash 100% Water @ 100°F (38°C) for 5 min, drain.

Neutralization 100% Water @ 100°F (38°C)
Add 25% float of a water solution of 1.25% sodium bicarbonate through the gudgeon
Run @ 16 rpm for 60 min, drain.
Target pH = 5.

Wash 100% Water @ 100°F (38°C) for 5 min, drain.

Retanning "A" 100% Water @ 80°F (26°C)
10% DLE Syntan
2% Baysyтан NNOL
Run @ 16 rpm for 60 min, drain.

Wash 100% Water @ 130°F (54.5°C) for 5 min, drain.

Retanning "B" 100% Water @ 80°F (26°C)
6% DLE Syntan
2% Baysyтан NNOL
4% Wattle
Run @ 16 rpm for 60 min, drain.

Wash 100% Water @ 130°F (54.5°C) for 5 min, drain.

Fatliquoring 75% Water @ 80°F (26°C)
5% Atlasol CAM
1% Eureka 400R
25% Water @ 80°F (26°C)
Run @ 16 rpm for 30 min.
2% Atlason 310L
10% Water @ 80°F (26°C)
Run @ 16 rpm for 10 min.
Haul and horse overnight covered with plastic.

Dyeing 100% Water @ 130°F (54.5°C)
1% Ammonium hydroxide
Run for 10 min.
1.5% Daxad 17 LPH
Run for 5 min.
4% Dye
Run for 90 min.

Dye fixation 1% Formic acid. Make 3 shots, one every 10 min.
1% Formic acid
Run for 15 min, target pH = 3.6.
0.75% Avalanfixb
Run for 10 min.

The 14 sides were then divided into 4 pieces, numbered 1 to 4 from tail to neck. Pieces 1 and 2 were retanned with a syntan, and pieces 3 and 4 were retanned with a vegetable retanning agent, i.e., wattle. These processes were done in conventional drums, in two main batches: right and left sides pieces, following the process listed above. Pieces 2 and 3 were dyed separately. The dyeing process is also described above.

All the pieces were set out, and vacuum dried, and left horsed up overnight to dry. They were rewet and put into plastic bags for one day, and they were staked twice. No finishing operations were done to the hides, which were kept in a shelf in the conditioned room (temperature and moisture) for at least 5 days.

After this period of time, 5 samples were taken of each piece of leather both perpendicular and parallel to the backbone. Every sample was weighed and analyzed for moisture. Their thickness along the testing area of the samples was averaged. And, finally, the tensile strength was determined on each of them.

Analyses. For moisture determination, the samples were weighed into dry, tared porcelain dishes. The samples were dried for 17 hrs at 105°C. They then were cooled in a desiccator and weighed. For ash determination, the dried samples were ashed at 600°C for two hours. The samples were cooled in a desiccator and weighed. These analytical methods were described in a previous publication.²⁹

Chromium was determined on a Perkin Elmer Atomic Absorption Spectrophotometer, Model 3300 (Norwalk, CT).³⁰ Solid samples were weighed into appropriate flasks that were fitted with standards joints, 2N HCL (75 mL) was added, and the samples were hydrolyzed for 4 hrs. The hydrolyzed samples were filtered into volumetric flasks and made up to volume. They were run on the AA after dilution so that the concentration would be between 1 and 10 ppm. Percent chromium and percent chromium oxide were calculated. For liquid samples, the solutions were well mixed and chromium was determined by aspirating the solution directly into the flame of the Atomic Absorption Spectrophotometer, or after the appropriate dilution.

Total Kjeldahl Nitrogen (TKN) was determined by the semi-micro Kjeldahl method. Solid samples were weighed to the nearest 50 mg and liquid samples were measured to 1 mL and transferred to a 30 mL digestion flask. Digestion catalyst (1.2 g), a few boiling chips and sulfuric acid (2 mL) were added. The samples were digested for two hours. The samples were carefully transferred to the filling funnel and NaOH solution (10 mL) was added. The mix was distilled to a 125 mL Erlenmeyer flask containing boric acid saturated solution (10 mL). The samples were titrated with standardized HCl to the gray endpoint.

For fat determination, samples were weighed into appropriate flasks and 6N HCl (75 mL) was added. The samples were hydrolyzed for 2 hrs. The hydrolysate was transferred to a separatory funnel and the fat was extracted with chloroform. The chloroform layer was added to dry, tared crystallizing dishes, the chloroform was evaporated and the samples were dried for 16 hrs at 60°C. The samples were cooled in a desiccator and weighed, and percent fat was calculated.

Shrinkage temperature of wet-blue samples was determined in a shrink-temperature pressure apparatus as described by Fein et al.³¹ One specimen of each wet sample with size 7/32" x 2-1/4" (5.6 x 57.2 mm; any thickness) was cut. The specimens were inserted into the appropriate holders, and placed into the bath. The water was heated (the rate of rise of temperature was maintained at 3°-3-1/2°C per minute) and the temperature at the first definite sign of shrinking was recorded.

For physical tests of the leather, five specimens parallel to the backbone and five perpendicular to the backbone were cut with a hydraulic pattern cutter (Clicker) (Sloan Machinery Co., Lynn, MA) for each piece of leather.³² The thickness of each specimen was measured with a Randall-Stickney dead-weight (Waltham, MA)³³ at three points. The moisture content was determined by a leather moisture meter (Delmhorst Instrument Co., Towaxo, NJ). Tensile strength of the samples was performed with an INSTRON model 1122 tensile strength machine (Canton, MA). All the data were collected and processed by an Instron series IX automated materials testing system version 5. The tensile strength of leather was measured at 23°C and 50% RH with a gauge length of 50 mm.

RESULTS AND DISCUSSION

Treatment of chrome cake. In Part I of this series,²⁸ the demonstration of the isolation of protein products from chrome cake on a pilot plant scale was described. The objective of that experiment was to isolate enough chrome cake for chemical purification, and reuse in the tanning trials described here.

The chrome shavings used as raw material for the chrome cake production were obtained from a commercial tannery in two different drums (A and B, Table I). They were analyzed for pH, moisture, ash, TKN, fat and chromium and the results are presented in Table I. As can be seen, the pH indicates that the chrome shavings in the drums were different so they were well homogenized and divided into four different batches. All the other values were as expected from this kind of waste.

The process used to isolate protein products was repeated four times (batches 1 to 4, Tables II and III). This treatment was carried out in a conventional pilot plant tanning drum (Dosemat, Dose Maschinebau GmbH, Lichtenau, Germany), and the filtering operations were accomplished in a manual filter press (Model AA, Serfilco, Ltd., Glenview, IL). The reproducibility of the process and the chemical and physical properties of the protein products isolated were presented in a previous paper.²⁸ The final solid product, the chrome cake, was the raw material for the process described in the present paper.

Tables II and III present the chemical analyses of the chrome cake, that is, moisture, ash, nitrogen, fat and chrome content. Due to the heterogeneous nature of these products, two samples were taken from different locations of the container of each filtration (the capacity of the filter press was less than that of the drum, so that at the end of each

TABLE I
Analyses of Chrome Shavings^a

Parameter	A	B
<i>pH</i>	3.45 (0.01) ^{b,c}	3.87 (0.05) ^{b,c}
<i>Moisture</i> ^d	53.12 (0.62)	50.52 (0.54)
<i>Ash</i> ^{d,e}	10.33 (0.40)	10.52 (0.29)
<i>TKN</i> ^{d,e,f}	16.45 (0.72)	16.59 (2.74)
<i>Cr₂O₃</i> ^{d,e}	3.27 (0.38)	3.01 (0.24)
<i>Fat</i> ^{d,e}	0.65 (0.06)	0.86 (0.17)

a Chrome shavings A and B came from a conventional chrome tannage in two different drums.

b Mean (Standard Deviation).

c N = 3 where N = number of replicates for each sample.

d Expressed as percentage.

e Moisture free basis.

f Ash free basis.

TABLE II
Chemical Properties of Chrome Cake

Parameter	Batch No. 1	Batch No. 2	Batch No. 3	Batch No. 4	Aver.	StdDev
<i>Moisture</i> ^{a,b,c}						
Filtration 1	82.37 (0.26)	82.97 (0.89)	81.09 (1.76)	79.81 (0.71)		
	81.89 (0.09)	82.56 (0.40)	82.36 (0.29)	81.67 (0.56)		
Filtration 2	85.52 (0.75)	82.71 (0.35)	84.15 (0.29)	83.97 (0.28)		
	84.72 (0.12)	83.06 (0.23)	83.80 (0.48)	84.20 (0.60)		
Average	83.63	82.83	82.85	82.41	82.93	0.51
<i>Total ash</i> ^{a,b,c,d}						
Filtration 1	38.15 (0.87)	41.99 (1.57)	40.46 (1.34)	40.14 (0.76)		
	39.83 (0.31)	43.47 (0.39)	41.25 (0.58)	40.37 (0.66)		
Filtration 2	41.69 (2.71)	40.52 (0.06)	41.58 (0.28)	42.12 (1.62)		
	44.03 (0.32)	42.27 (0.61)	41.86 (0.45)	40.25 (0.23)		
Average	40.93	42.06	41.29	40.72	41.25	0.59

a Mean (Standard Deviation).

b N = 3 where N = number of replicates for each sample.

c Expressed as percentage.

d Moisture free basis.

TABLE III
Chemical Properties of Chrome Cake

Parameter	Batch No. 1	Batch No. 2	Batch No. 3	Batch No. 4	Aver.	StdDev
<i>TKN</i> ^{a,b,c,d,e}						
Filtration 1	11.87 (0.51)	10.21 (0.47)	11.11 (0.81)	11.45 (1.09)		
	12.79 (0.30)	9.64 (0.85)	11.26 (0.85)	7.91 (0.21)		
Filtration 2	11.99 (0.83)	12.41 (0.42)	10.27 (0.92)	10.11 (1.32)		
	10.86 (0.39)	12.82 (0.46)	11.07 (0.52)	8.27 (0.21)		
Average	11.88	11.27	10.93	9.44	10.88	1.04
<i>Fat</i> ^{a,b,c,d}						
Filtration 1	0.82 (0.06)	0.49 (0.01)	0.49 (0.06)	0.40 (0.02)		
	0.79 (0.02)	0.53 (0.07)	0.34 (0.01)	0.44 (0.05)		
Filtration 2	0.33 (0.05)	0.59 (0.00)	0.41 (0.14)	0.38 (0.03)		
	0.38 (0.02)	0.49 (0.10)	0.27 (0.03)	0.37 (0.09)		
Average	0.58	0.53	0.38	0.40	0.47	0.10
<i>Chrome oxide</i> ^{a,b,c,d}						
Filtration 1	7.21 (0.33)	8.46 (0.06)	7.84 (0.30)	7.49 (0.13)		
	6.51 (0.05)	8.58 (0.16)	8.08 (0.03)	7.09 (0.32)		
Filtration 2	8.23 (0.08)	10.37 (0.05)	7.46 (0.93)	7.14 (0.23)		
	7.19 (0.16)	10.19 (0.82)	8.58 (0.21)	6.78 (0.14)		
Average	7.29	9.40	7.99	7.13	7.95	1.04

a Mean (Standard Deviation).

b N = 3 where N = number of replicates for each sample.

c Expressed as percentage.

d Moisture free basis.

e Ash free basis.

TABLE IV
Mass Balance of Chrome Cake Treatment

Parameter	% Recovery
Protein precipitation step	96.58
Chrome precipitation step	96.27
Total material balance	94.59

run the material from the run was filtered in two batches), meaning that for each batch, four samples of chrome cake were obtained. For each analysis the mean and the standard deviation are given and for each parameter the average and the standard deviation of the four batches were calculated. The analyses *per se* and the repeatability of the analyses in these experiments were quite good, as indicated by the standard deviations.

The process to purify the chrome cake is presented in Figure 1. The chrome cake was dissolved with concentrated sulfuric acid; the dissolution was started in two large buckets with hand agitation outdoors, and finished in a conventional pilot plant tanning drum where the pH adjustment was done with a 50% (w/w) solution of sodium hydroxide.

The suspended chromium solution was heated to 70°C and not to the boiling point, because the temperature in the tanning drum would not go any higher; therefore the solution was kept at this temperature for two hours instead of the 10 min recommended in the literature.²⁷

After chrome precipitation, the recovered chromium oxide settled within two or three hours. It did not require an overnight settling step.²⁷

The purified chromium was filtered in a manual press, twice. Both filtrate and wash streams and solid cake were mixed together. One sample of each of these fractions and a sample of the protein filtered in the Büchner porcelain funnels were taken and analyzed. The purified chromium was washed copiously with water.

The process was performed only once, and the mass balance is shown in Table IV. The protein precipitation step, the chrome precipitation step and the total material balance of the process give a recovery of 94% or above.

The chemical properties of the samples obtained in this test are presented in Tables V and VI. The solid samples recovered (Table V) were the filtered protein, to be discharged, and the purified chromium, to be used in the tanning trials. It is remarkable that the filtered protein presented a high nitrogen and fat content, and a very low chrome content, though the purified chrome presented a low nitrogen content, a nil fat content and a high chromium content. The liquid samples corresponding to the two stages of the chromium filtration and wash are shown in Table VI.

Adjustment of basicity. Chromic sulfate has only a very slight tanning capability. Only basic chrome sulfates, in which some sulfate anions are replaced by hydroxyl anions, are capable of tanning. The tanning effect, often called the

astringency, increases with the fraction of OH groups associated with the chromium until, above a basicity of approximately 57%, the chrome tanning materials start to become insoluble and precipitate.³⁴

The basicity is expressed in % Schorlemmer and indicates the percentage of valencies in the chromium(III) compounds that are bound to OH groups. Although normal commercial chrome tanning materials mostly have 33% basicity, products with 42% and 50% basicity are also available. The basicity can be increased or reduced by adding alkalis or acids respectively.

In the present work, basicity was adjusted to 33% by dissolving the purified precipitated chromium with sulfuric acid to pH 2.3.

Tanning trials. Matched sides trials were set up to test the tanning performance of the recovered chromium. Seven fresh cattle hides were collected from a commercial slaughter house. They were processed as follows: halved, trimmed, fleshed, soaked, unhaired, relimed and delimed, bated and pickled in two groups in the pilot plant tannery at ERRC, using the process described in the experimental part. Table VII shows the weights of all sides fleshed raw and after pickling.

The right sides from tail to neck were tanned with the commercial chrome powder, Oxochrome, serving as controls. The left sides were tanned with mixtures of this commercial chrome and the recovered chrome solution, from 0 % to 100 % of recovered chrome. The control sides were tanned in three different groups, and the recovered sides were tanned singly.

The tanning operation of the left sides was done with a relatively short float (75%), 5% salt, 0.75% of sodium formate, 0.1% of Busan 30 and the tanning mixture (as in the standard process). The tanning mixture consisted of a certain amount of Oxochrome, a certain volume of the prepared tanning solution and water to reach the 75% float.

The tanning operation consisted in leaving the hides 4 hours in the chrome bath, while the temperature was raised from 80 to 110°F, and the drum was running at 16 rpm. Basification was done very slowly with small additions of sodium bicarbonate, and pH was continuously monitored. The process was stopped at pH 3.8-3.9; the whole process lasted between 9 to 11 hours. The sides were horsed-up and left overnight. The basification curves of all the tanning batches are presented in Figures 2 and 3. Figure 2 shows the three batches of controls, and Figure 3 the seven batches of trials with recovered chromium.

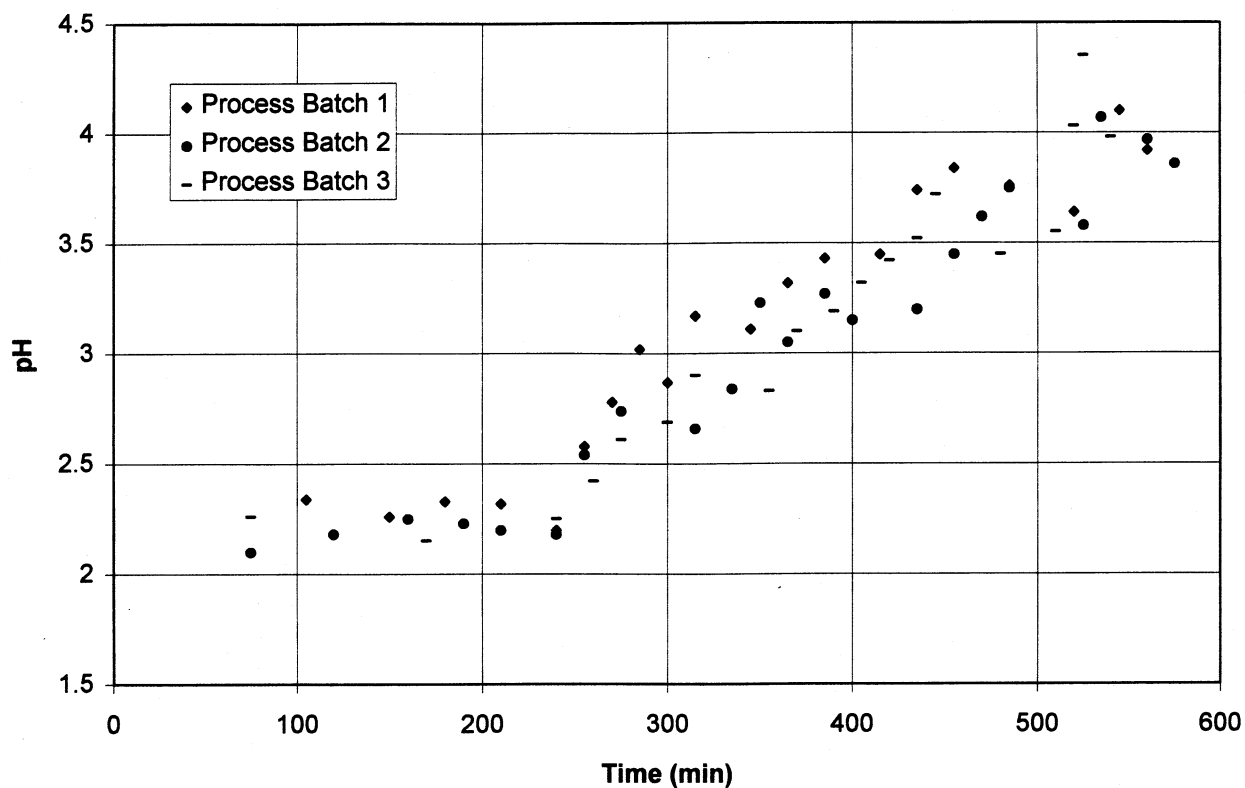


FIGURE 2. — Basification curves for control side trials.

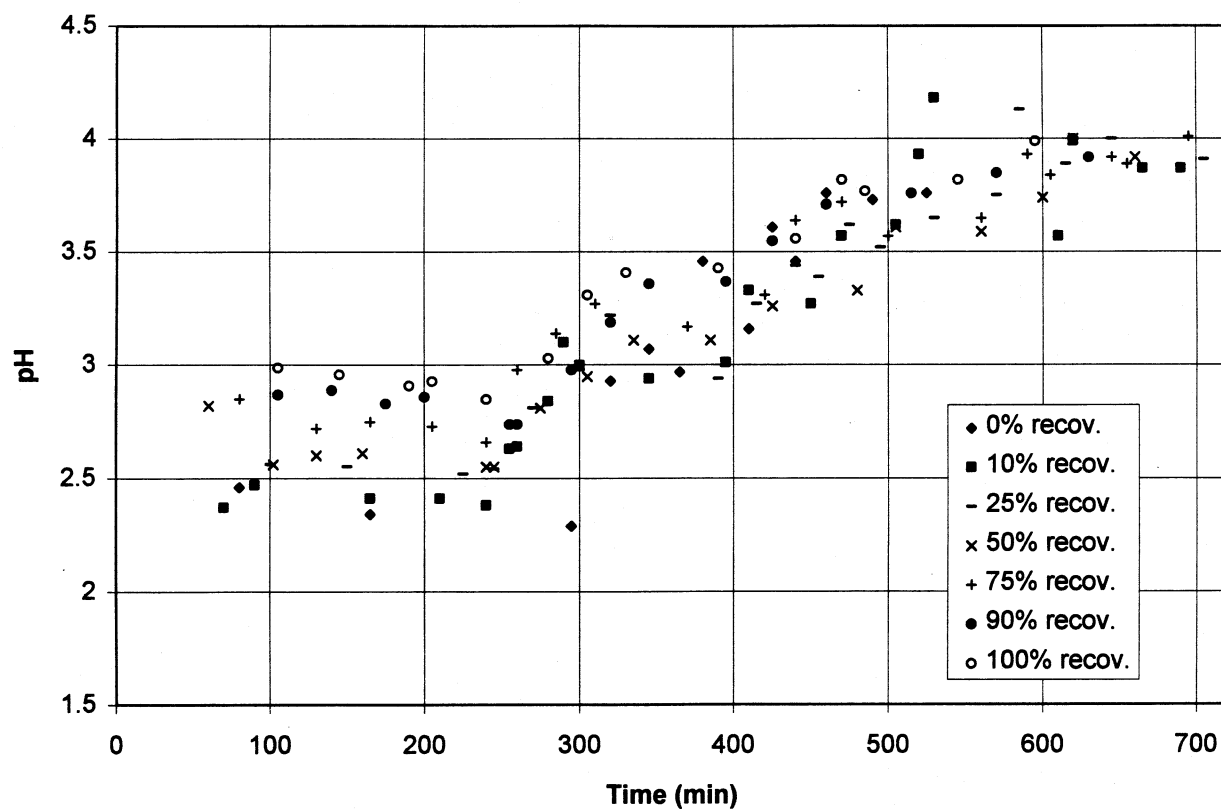


FIGURE 3. — Basification curves for recovered chrome side trials. (Recov. = percentage of recovered chromium in total chromium used for tanning).

TABLE V
Chemical Properties of Solid Samples from Chrome Cake Treatment

Parameter	Filtered Protein	Purified Chromium
<i>Moisture</i> ^{a,b,c}	60.35 (0.41)	78.21 (0.51)
<i>Total ash</i> ^{a,b,c,d}	32.27 (1.25)	72.94 (0.44)
<i>TKN</i> ^{a,b,c,d,e}	10.65 (0.96)	2.20 (0.14)
<i>Fat</i> ^{a,b,c,d}	4.60 (0.19)	0.0023 (0.00)
<i>Chromium</i> ^{a,b,c,d}	0.68 (0.00)	14.15 (0.48)

a Mean (Standard Deviation).

b N = 3 where N = number of replicates for each sample.

c Expressed as percentage.

d Moisture free basis.

e Ash free basis.

TABLE VI
Chemical Properties of Liquid Samples from Chrome Cake Treatment

Parameter	Filtrate	Wash
<i>pH</i>	9.10	8.20
<i>Total solids</i> ^{a,b,c}	19.55 (0.07)	10.47 (0.04)
<i>Total ash</i> ^{a,b,c,d}	81.95 (0.47)	90.95 (0.62)
<i>TKN</i> ^{a,b,c,d,e}	8.24 (0.20)	6.15 (0.08)
<i>Chrome</i> ^{a,b,c,d}	17.92 (0.00)	14.33 (0.00)

a Mean (Standard Deviation).

b N = 3 where N = number of replicates for each sample.

c Expressed as percentage.

d Moisture free basis.

e Ash free basis.

TABLE VII
Weight of Hides to be Tanned with Recovered Chrome

Hide	Raw Weight (kg)			Pickled Weight (kg)		
	Left	Right ^a	Total	Left	Right ^a	Total
1	16.94	15.40	32.34	14.70	14.10	28.80
2	16.08	16.72	32.80	14.25	13.85	28.10
3	15.90	15.08	30.99	13.80	12.75	26.55
4	13.68	13.09	26.77	11.70	12.15	23.85
5	13.68	13.23	26.91	11.65	11.45	23.10
6	11.28	12.23	23.51	11.15	9.80	20.95
7	10.74	10.42	21.16	9.40	9.45	18.85

a Right sides (from tail to neck) were considered controls.

TABLE VIII

Chemical Analyses of Matched Sides of Wet Blue Tanned with Recovered Chrome

Recovered Chrome ^a	<i>Moisture</i> ^{b,c,d}		<i>Ash</i> ^{b,c,d,e}		<i>Chrome oxide</i> ^{b,c,d,e}	
	Control	Recov.	Control	Recov.	Control	Recov.
0%	55.19 (0.26)	53.88 (0.18)	11.94 (0.24)	11.68 (0.12)	4.50 (0.24)	4.54 (0.21)
10%	52.08 (0.22)	54.25 (0.26)	12.38 (0.78)	11.37 (0.23)	3.76 (0.64)	3.79 (0.08)
25%	48.62 (0.23)	53.07 (0.33)	11.90 (0.36)	10.14 (0.25)	5.22 (0.07)	3.91 (0.09)
50%	53.11 (0.37)	55.39 (0.88)	11.70 (0.36)	13.25 (0.26)	4.34 (0.68)	4.12 (0.22)
75%	50.61 (0.70)	53.17 (0.65)	11.23 (0.35)	11.41 (0.34)	4.86 (0.80)	3.72 (0.12)
90%	53.41 (0.36)	53.02 (0.04)	11.40 (0.27)	11.08 (0.06)	5.47 (0.05)	3.56 (0.09)
100%	53.76 (0.41)	52.64 (0.05)	11.84 (0.15)	11.60 (0.38)	3.48 (0.52)	3.69 (0.04)
Average	52.40	53.63	11.77	11.50	4.52	3.90
Std.Dev.	2.19	0.95	0.38	0.93	0.73	0.33

a Percentage of recovered chromium in total chromium used for tanning.

b Mean (Standard Deviation).

c N = 3 where N = number of replicates for each sample.

d Expressed as percentage.

e Moisture free basis.

TABLE IX

Shrinkage Temperature of Matched Sides of Wet Blue Tanned with Recovered Chrome

Recovered Chrome ^a	Control ^{b,c}	Recov. ^{b,c}
0%	100	100
10%	100	100
25%	101	98.5
50%	101	98
75%	101	97.5
90%	101	100
100%	101	97.5

a Percentage of recovered chromium in total chromium used for tanning.

b N=1 where N=number of replicates for each sample.

c °C.

TABLE X
Tensile Strength Test Results of Matched Sides of Crust Leather Tanned
with Recovered Chrome and Retanned with a Syntan and Not Dyed

Recovered Chrome ^a	Thickness (mm) ^{b,c}		Max. Strain (%) ^{b,c}		Max. Load (N) ^{b,c}		Max. Stress (MPa) ^{b,c}	
	Control	Recov.	Control	Recov.	Control	Recov.	Control	Recov.
<i>Parallel</i>								
0%	1.96 (0.09)	2.02 (0.08)	88.9 (2.7)	80.1 (5.6)	529.8 (19.1)	514.2 (74.8)	21.35 (1.39)	20.02 (2.86)
10%	2.20 (0.05)	2.35 (0.05)	91.3 (3.0)	110.8 (7.8)	663.2 (35.4)	742.4 (29.7)	23.77 (1.51)	24.85 (1.34)
25%	2.16 (0.03)	2.13 (0.07)	101.3 (8.0)	102.7 (15.3)	429.6 (63.2)	427.8 (47.0)	15.67 (2.33)	15.70 (2.03)
50%	2.16 (0.09)	2.18 (0.03)	75.3 (7.4)	70.2 (3.7)	425.2 (75.7)	570.9 (92.9)	15.46 (2.06)	20.55 (2.95)
75%	2.19 (0.02)	2.39 (0.05)	83.2 (2.5)	108.9 (4.5)	553.5 (52.2)	600.7 (51.6)	19.87 (1.95)	19.62 (1.62)
90%	2.06 (0.07)	2.21 (0.06)	69.8 (8.8)	70.9 (8.3)	479.1 (92.2)	583.4 (96.0)	18.14 (3.00)	20.75 (2.97)
100%	2.08 (0.07)	2.09 (0.06)	86.4 (4.4)	82.9 (8.8)	743.4 (53.8)	786.6 (32.2)	28.18 (1.39)	29.45 (0.72)
<i>Perpendicular</i>								
0%	1.91 (0.06)	1.92 (0.10)	94.6 (8.8)	102.0 (3.3)	474.6 (60.9)	517.2 (23.3)	19.37 (2.16)	21.07 (0.57)
10%	2.19 (0.02)	2.28 (0.04)	100.4 (5.0)	107.4 (11.8)	598.8 (25.1)	605.5 (17.5)	21.53 (0.85)	20.85 (0.67)
25%	2.18 (0.06)	2.23 (0.06)	108.6 (7.1)	98.2 (5.5)	459.7 (43.3)	578.8 (72.3)	16.58 (1.36)	20.45 (2.01)
50%	2.20 (0.06)	2.07 (0.06)	95.7 (1.3)	92.6 (6.0)	521.6 (19.7)	620.0 (47.4)	18.50 (0.51)	23.63 (1.97)
75%	2.21 (0.11)	2.15 (0.10)	93.0 (5.9)	108.0 (7.2)	560.4 (87.9)	591.1 (87.9)	19.97 (2.17)	21.45 (2.24)
90%	2.02 (0.04)	2.10 (0.08)	93.5 (4.4)	78.8 (5.8)	439.3 (33.8)	561.4 (59.2)	17.05 (1.76)	21.04 (1.56)
100%	2.08 (0.03)	2.18 (0.07)	90.5 (5.5)	85.2 (7.4)	725.5 (72.7)	871.9 (36.9)	27.36 (2.69)	31.63 (1.68)

a Percentage of recovered chromium in total chromium used for tanning.

b Mean (Standard Deviation).

c N = 5 where N = number of replicates for each sample.

TABLE XI
Tensile Strength Test Results of Matched Sides of Crust Leather Tanned
with Recovered Chrome and Retanned with a Syntan and Dyed

Recovered Chrome ^a	Thickness (mm) ^{b,c}		Max. Strain (%) ^{b,c}		Max. Load (N) ^{b,c}		Max. Stress (MPa) ^{b,c}	
	Control	Recov.	Control	Recov.	Control	Recov.	Control	Recov.
<i>Parallel</i>								
0%	2.15 (0.05)	2.34 (0.04)	73.6 (5.0)	78.6 (7.8)	739.6 (42.3)	869.9 (35.5)	27.14 (1.99)	29.26 (1.43)
10%	2.07 (0.04)	2.30 (0.04)	76.4 (2.0)	91.2 (3.5)	896.6 (53.3)	928.0 (39.0)	34.02 (1.45)	30.83 (1.12)
25%	2.26 (0.04)	2.15 (0.01)	83.2 (1.4)	84.7 (3.9)	763.6 (49.0)	763.0 (82.7)	17.15 (1.75)	28.01 (3.12)
50%	2.14 (0.04)	2.17 (0.06)	65.3 (3.7)	79.3 (5.0)	682.6 (55.7)	794.7 (40.6)	25.25 (1.72)	28.90 (1.63)
75%	2.06 (0.03)	2.40 (0.03)	71.8 (3.3)	90.9 (5.6)	786.6 (66.9)	915.7 (79.4)	30.08 (2.27)	29.98 (2.39)
90%	1.99 (0.06)	2.03 (0.03)	66.9 (4.5)	84.5 (4.9)	654.9 (57.8)	709.6 (31.1)	25.97 (2.15)	27.59 (1.47)
100%	2.13 (0.05)	2.30 (0.06)	67.2 (2.3)	77.4 (4.4)	1056.0 (27.0)	1131.0 (19.0)	39.01 (0.64)	38.74 (1.54)
<i>Perpendicular</i>								
0%	2.21 (0.05)	2.24 (0.05)	60.8 (4.7)	90.4 (5.8)	474.8 (89.8)	702.9 (46.2)	22.90 (1.65)	23.64 (1.62)
10%	1.99 (0.16)	2.18 (0.03)	52.0 (3.3)	87.8 (5.0)	515.4 (126.1)	553.7 (30.3)	21.81 (1.07)	20.00 (1.15)
25%	2.35 (0.07)	2.05 (0.05)	60.7 (3.5)	93.5 (7.3)	538.9 (54.6)	546.0 (21.4)	18.32 (1.33)	20.99 (0.49)
50%	2.16 (0.02)	2.22 (0.07)	75.0 (5.4)	83.7 (3.2)	648.5 (63.8)	638.3 (47.4)	22.63 (0.69)	22.66 (1.52)
75%	2.31 (0.07)	2.42 (0.11)	79.8 (1.8)	85.2 (4.4)	616.2 (36.0)	711.5 (34.2)	23.00 (1.91)	23.21 (1.21)
90%	2.22 (0.06)	2.15 (0.04)	72.8 (6.5)	80.7 (4.4)	596.3 (43.8)	670.3 (61.4)	22.17 (1.52)	24.60 (1.57)
100%	2.23 (0.12)	2.35 (0.04)	60.2 (4.3)	75.0 (6.0)	838.7 (51.8)	1022.0 (97.5)	30.22 (1.08)	34.18 (2.72)

a Percentage of recovered chromium in total chromium used for tanning.

b Mean (Standard Deviation).

c N = 5 where N = number of replicates for each sample.

TABLE XII

Tensile Strength Test Results of Matched Sides of Crust Leather Tanned with Recovered Chrome and Retanned with a Syntan and Wattle, and Not Dyed

Recovered Chrome ^a	Thickness (mm) ^{b,c}		Max. Strain (%) ^{b,c}		Max. Load (N) ^{b,c}		Max. Stress (MPa) ^{b,c}	
	Control	Recov.	Control	Recov.	Control	Recov.	Control	Recov.
<i>Parallel</i>								
0%	2.50 (0.10)	1.97 (0.05)	134.6 (10.3)	55.7 (4.2)	619.4 (129.7)	641.9 (97.2)	19.52 (3.39)	25.67 (3.41)
10%	2.19 (0.15)	2.12 (0.13)	92.3 (5.8)	80.8 (3.6)	624.7 (44.5)	797.4 (66.0)	22.53 (2.28)	29.32 (1.97)
25%	2.15 (0.15)	1.84 (0.13)	111.0 (17.2)	75.8 (8.9)	381.8 (25.6)	453.6 (79.4)	14.03 (0.91)	19.03 (1.97)
50%	1.95 (0.04)	2.09 (0.10)	65.8 (6.1)	72.4 (5.0)	553.7 (40.2)	733.6 (59.4)	22.36 (1.97)	27.76 (3.08)
75%	2.04 (0.21)	1.98 (0.11)	64.5 (6.2)	50.9 (3.9)	498.9 (169.9)	600.2 (37.7)	19.63 (4.84)	23.77 (2.23)
90%	1.98 (0.13)	2.29 (0.16)	102.8 (8.1)	62.6 (11.0)	587.4 (35.5)	1053.0 (102)	23.42 (0.73)	36.28 (2.43)
100%	2.18 (0.15)	2.67 (0.10)	110.8 (10.0)	77.8 (2.4)	612.6 (126.3)	1636.0 (69.0)	21.98 (3.15)	48.90 (1.32)
<i>Perpendicular</i>								
0%	2.61 (0.07)	2.18 (0.08)	65.4 (9.6)	70.1 (12.7)	691.0 (181.5)	549.9 (168.6)	20.78 (4.98)	19.71 (5.58)
10%	2.44 (0.12)	2.04 (0.49)	73.3 (7.2)	94.0 (6.1)	558.7 (119.9)	671.9 (79.6)	17.97 (3.37)	27.99 (7.65)
25%	2.18 (0.07)	1.95 (0.09)	71.9 (11.5)	67.4 (12.3)	432.9 (64.2)	410.0 (113.0)	15.79 (2.52)	16.41 (3.97)
50%	1.84 (0.06)	2.62 (0.37)	102.9 (10.1)	83.4 (4.2)	384.4 (29.1)	1022.0 (122)	16.35 (0.75)	26.17 (3.81)
75%	2.00 (0.06)	1.96 (0.12)	103.8 (12.2)	108.7 (21.3)	300.8 (28.5)	398.2 (72.4)	11.80 (0.78)	15.82 (3.21)
90%	1.83 (0.04)	2.09 (0.02)	70.0 (1.0)	107.2 (4.1)	466.3 (35.9)	621.3 (64.7)	20.02 (1.44)	23.37 (2.32)
100%	2.07 (0.07)	2.48 (0.09)	66.5 (3.3)	66.4 (6.3)	592.6 (105.5)	803.7 (109.7)	22.52 (3.15)	25.50 (3.15)

a Percentage of recovered chromium in total chromium used for tanning.

b Mean (Standard Deviation).

c N = 5 where N = number of replicates for each sample.

TABLE XIII

Tensile Strength Test Results of Matched Sides of Crust Leather Tanned with Recovered Chrome and Retanned with a Syntan and Wattle, and Dyed

Recovered Chrome ^a	Thickness (mm) ^{b,c}		Max. Strain (%) ^{b,c}		Max. Load (N) ^{b,c}		Max. Stress (MPa) ^{b,c}	
	Control	Recov.	Control	Recov.	Control	Recov.	Control	Recov.
<i>Parallel</i>								
0%	2.20 (0.02)	2.35 (0.03)	83.4 (4.9)	90.6 (2.4)	545.4 (21.7)	681.6 (38.7)	19.48 (0.73)	22.79 (1.09)
10%	1.96 (0.09)	2.25 (0.04)	67.5 (8.5)	86.0 (6.4)	447.1 (99.4)	619.0 (49.3)	17.85 (3.16)	21.37 (1.65)
25%	2.31 (0.12)	2.27 (0.05)	84.0 (4.8)	81.6 (4.2)	587.2 (93.5)	578.8 (57.1)	19.96 (2.50)	20.07 (1.61)
50%	2.07 (0.06)	2.50 (0.07)	65.7 (3.7)	122.3 (4.5)	581.0 (58.4)	669.5 (51.6)	22.18 (2.10)	21.07 (1.57)
75%	2.29 (0.06)	2.40 (0.07)	69.2 (4.0)	90.6 (10.1)	663.5 (116.8)	685.4 (69.7)	22.76 (3.68)	22.43 (1.85)
90%	2.20 (0.06)	2.32 (0.04)	76.1 (3.0)	89.8 (1.6)	598.9 (35.4)	716.3 (4.5)	21.36 (0.87)	24.07 (0.25)
100%	2.34 (0.03)	2.54 (0.14)	74.3 (3.2)	57.6 (4.3)	826.5 (55.3)	1228.0 (179)	27.75 (1.58)	38.06 (2.08)
<i>Perpendicular</i>								
0%	2.21 (0.03)	2.42 (0.03)	74.2 (3.3)	70.4 (5.5)	641.6 (47.5)	768.6 (96.6)	16.90 (2.96)	24.99 (3.38)
10%	2.05 (0.08)	2.24 (0.04)	71.5 (2.7)	59.9 (5.2)	569.4 (41.6)	731.5 (45.3)	20.28 (3.94)	25.76 (1.44)
25%	2.10 (0.10)	2.37 (0.06)	85.8 (3.5)	58.0 (4.0)	479.4 (54.3)	605.7 (28.2)	18.05 (1.29)	20.12 (0.79)
50%	2.16 (0.07)	2.26 (0.07)	77.8 (4.8)	69.5 (7.6)	621.8 (23.0)	784.6 (32.9)	23.64 (2.28)	27.33 (1.32)
75%	2.18 (0.06)	2.41 (0.07)	67.5 (3.6)	84.7 (0.7)	639.0 (68.8)	736.5 (79.4)	21.01 (1.11)	24.26 (2.07)
90%	2.11 (0.02)	2.33 (0.03)	69.9 (4.7)	62.8 (3.9)	593.1 (36.4)	754.7 (40.2)	21.13 (1.88)	25.53 (1.33)
100%	2.17 (0.05)	2.77 (0.06)	65.5 (2.4)	56.4 (1.6)	832.9 (36.5)	1551.0 (107)	29.57 (1.46)	44.11 (2.14)

a Percentage of recovered chromium in total chromium used for tanning.

b Mean (Standard Deviation).

c N = 5 where N = number of replicates for each sample.

One sample was taken from each side, a strip 2 cm wide and 30 cm long, parallel to the backbone in the tail area. Strips were analyzed for moisture, ash, and chromium content, and the results are shown in Table VIII. Moisture and ash values of all the wet blue samples are very similar. Comparing the chromium content of the matched sides, no significant differences can be seen in hides with 0, 10, 50, and 100% recovered chromium. Hides with 25, 75 and 90% recovered chromium show important differences that cannot be correlated with any factor. However, chromium content in all cases is above 3.5%. The factor that seems to have more influence on the chromium uptake is the hide itself. This could explain why sides that were tanned in the same drum (such as the control for 10 and 50% recovered chromium, or the control for 25, 75 and 100% recovered chromium) have very different chromium contents. Another important factor is that the wet blue samples were cut before splitting, so they had different thicknesses and densities.

The shrinkage temperatures of these pieces of leather were also analyzed, and the results are shown in Table IX. While all the controls have a value of 100-101°C, the recovered chromium sides show more variability but with all the values above 97°C.

The 14 sides were then divided into 4 pieces, numbered 1 to 4 from tail to neck. Pieces 1 and 2 were retanned with a syntan, and pieces 3 and 4 were retanned with a vegetable retanning agent, i.e., wattle. Pieces 2 and 3 were dyed separately. No finishing operations were done to the hides, which were kept on a shelf in the conditioned room (temperature and moisture) for at least 5 days. After this period of time, 5 samples were taken of each piece of leather both perpendicular and parallel to the backbone. Every sample was weighed and analyzed for moisture. Their thicknesses along the testing area of the samples were averaged. Finally, the tensile strength was measured on each of them.

Tables X to XIII show the results of the tensile strength test. The data presented summarize the tests for the crust leather tanned with different amounts of recovered chromium. The maximum strain and the maximum stress measures were evaluated statistically, the values were analyzed to compare the control vs. the recovered values and the significances were determined at the 0.05 significance level.

When the leather was retanned with syntan and not dyed (Table X), only 35% of the samples showed significant differences between the control and the recovered values, and 80% of these differences presented an improvement of the test when recovered chromium was used. When the leather was retanned with syntan and dyed (Table XI), 80%

of the maximum strain values showed a significant difference, always with an increase when recovered chromium was used; 45% of the maximum stress values showed a significant difference with 85% of these differences being an increase when recovered chromium was used.

When the leather was retanned with syntan and wattle, the perpendicular and parallel samples showed different behavior. When the leather was not dyed (Table XII) the maximum strain of the parallel specimens presented a decrease in 85% of the samples when recovered chromium was used, but the maximum stress always showed a significant increase. The perpendicular specimens showed significant difference in only 35% of the samples, with an increase in 80% of them. When the leather was dyed (Table XIII), 80% of the samples presented a significant difference, being an increase when recovered chromium was used in all the results but the maximum strain of the perpendicular specimens.

These results indicate that when leather tanned with recovered chromium is retanned with syntan, the physical quality of the leather shows no reduction. When the leather is retanned with syntan and wattle, a reduction of some of the maximum strain values was observed using recovered chromium as tanning agent, but all the maximum stress values improved.

CONCLUSIONS

In Part I of this series, we demonstrated that the process to isolate gelatin and hydrolysate from chrome shavings is reproducible on a pilot plant scale. Enough chrome cake was isolated to be purified as described in this paper. A chemical process was used to purify the chrome cake. The mass balance of the process showed good recovery of chromium and protein at each step of the process. The purified chromium had low nitrogen and nearly no fat content. The chemical analyses of the leather in the wet blue stage and the physical tests in the crust stage indicated that it is possible to reuse the chrome recovered with this procedure in the tannery without a decrease in the quality of the leather.

ACKNOWLEDGMENTS

The authors acknowledge P. Samsó, T. Bosch, M. Tornos, S.M. Clauson and T.A. Dunn for their valuable contribution to the work presented in this paper. The authors are also grateful to M.D. McClintick and Dr. J.G. Phillips for their helpful comments.

REFERENCES

- Gauglhofer, J.; Environmental aspects of tanning with chromium. *J. Soc. Leather Technol. Chem.* **70**, 11-13, 1986.
- Anonymous; Chrome: Recycling versus recovery. *Leather* (Aug.), 28-30, 1993.
- Davis, M. H. and Scroggie, J. G.; Investigation of commercial chrome-tanning systems. Part III: Re-cycling of used chrome liquors. *J. Soc. Leather Technol. Chem.* **57**, 53-58, 1973.
- Davis, M. H. and Scroggie, J. G.; Investigation of commercial chrome-tanning systems. Part IV: Re-cycling of chrome liquors and their use as a basis for pickling. *J. Soc. Leather Technol. Chem.* **57**, 81-83, 1973.
- Davis, M. H. and Scroggie, J. G.; Investigation of commercial chrome-tanning systems. Part V: Re-cycling of chrome liquors in commercial practice. *J. Soc. Leather Technol. Chem.* **57**, 173-176, 1973.
- Burns, J. E., Colquitt, D. E., Davis, M. H. and Scroggie, J. G.; Investigation of commercial chrome-tanning systems. Part VI: Full-scale trials of chrome liquor recycling and the importance of salt concentration. *J. Soc. Leather Technol. Chem.* **60**, 106-112, 1976.
- Pierce, R., Thorstensen, T. C.; The recycling of chrome tanning liquors. *JALCA* **71**, 161-168, 1976.
- Barlow, J. R. and Ip, H. S. W.; Some properties of wet-blue leathers produced from recycled chrome tanning liquors. *J. Soc. Leather Technol. Chem.* **61**, 29-33, 1977.
- Arnoldi, H. W. and Covington, A. D.; Studies in chrome utilisation in UK tanneries. Part II. Chrome recycling systems. *J. Soc. Leather Technol. Chem.* **65**, 5-10, 1981.
- Sharp, B. W.; Chrome recycling. *JALCA* **76**, 24-34, 1981.
- Wada, K., Shirai, K. and Kubo, T.; Investigation on the recycling of spent chrome liquor from the viewpoint of chrome complex composition. *JALCA* **76**, 333-342, 1981.
- Boast, D. A.; An investigation into differences in properties of leathers produced from chrome recycling and conventional chrome tannage. *J. Soc. Leather Technol. Chem.* **73**, 164-167, 1989.
- Davis, M. H. and Scroggie, J. G.; Theory and practice of direct chrome liquor recycling. *Leder* **31**, 1-8, 1980.
- Cranston, R. W., Gleisner, R. W., Macoun, R. G., Simpson, C. M., Cowey, S. G. and Money, C. A.; The Total Recycling of Chromium and Salts in Tanning Liquors. *Proceedings of the IULTCS Centenary Congress*, **1**, 224-229, 1997.
- Andres, H.; Erfahrungen mit Chromrecycling. *Leder* **36**, 17-31, 1985.
- Boast, D. A.; Large scale chrome recovery from chrome wash liquors. *JALCA* **83**, 17-23, 1988.
- Feikes, L., Schmiedel, W., Schröder, D. and Stiegler, R.; 60 Jahre Chromrückgewinnung. *Leder* **33**, 84-87, 1982.
- Rutkowski, J. R., Kosinska, D. and Urbaniak, M. Studies on the Application of Maximum Amount of Chromium Recovered from Spent Tanning Liquors in the Process of Chrome Tanning. *Proceedings of the IULTCS Centenary Congress*, **1**, 262-266, 1997.
- Rajamani, S.; A Successful and Sustainable Chromium Recovery and Reuse System Using Magnesium Oxide and Sulphuric Acid in Tanneries. *Proceedings of the IULTCS Centenary Congress*, **1**, 294, 1997.
- Spahrmann, J.; Direct and indirect recycling of tannery waste water. *JALCA* **74**, 418-421, 1979.
- Cartier, J. E.; An ash stabilization process for the recovery and reuse of chromium from chrome-laden tannery waste and a treatment process for pollution control of tannery waste water. *JALCA* **75**, 322-330, 1980.
- Okamura, H. and Shirai, K.; Recovery of chromium from shavings by wet air oxidation. *JALCA* **71**, 173-179, 1976.
- Tancous, J. J., Bellingham, R., Kallenberger, W. and McDonell, A.; Conservation of chromium in the tanning industry. *JALCA* **76**, 164-175, 1981.
- Veeger, L.; Chrome recovery out of tannery wastes. *World Leather* **7**, 82, 1994.
- Taylor, M. M., Diefendorf, E. J., Thompson, C. J., Brown, E. M., Marmer, W. N. and Cabeza, L. F.; Extraction of value added byproducts from the treatment of chromium containing collagenous leather industry waste. *J. Soc. Leather Technol. Chem.* **81**, 5-15, 1996.
- Taylor, M. M., Diefendorf, E. J., Thompson, C. J., Brown, E. M., Marmer, W. N. and Cabeza, L. F.; Extraction of value-added by-products from the treatment of chromium-containing collagenous waste generated in the leather industry. *Bol. Téc. AQEIC* **47**, 124-150, 1996.

27. Okamoto, Y., and Katano, S.; Purified chromium compounds from waste liquid containing chromium. *Japan* **74** 16, 358, 1974.
28. Taylor, M. M., Cabeza, L. F., Carrió, R., DiMaio, G. L., Brown, E. M., Celma, P. J., Cot, J. and Marmer, W. N.; Processing of leather waste: Pilot scale studies on chrome shavings. Part I. Isolation and characterization of protein products and separation of chrome cake. *JALCA* **93**, 61-82, 1998.
29. Taylor, M. M., Diefendorf, E. J., Phillips, J. G., Fairheller, S. H., and Bailey, D. G.; Wet process technology I. Determination of precision for various analytical procedures. *JALCA* **81**, 4-18, 1986.
30. Taylor, M. M., Diefendorf, E. J., Marmer, W. N., Brown, E. M.; Effect of various alkalinity-inducing agents on chemical and physical properties of protein products isolated from chromium-containing leather waste. *JALCA* **89**, 221-228, 1994.
31. Fein, M. L., Harris, E. H., Jr., and Calhoun, R. R., Jr.; Report on shrink temperatures. Determination of Ts on suspended leather specimens. *JALCA* **55**, 15-30, 1965.
32. ALCA method E15, April 1953.
33. ALCA method E4, April 1953.
34. Anonymous; Tanning. Dyeing. Finishing. GK 765e, Bayer, Leverkusen, Germany.